



## Electronic and Vibration Spectra of Hydrogenated Carbon Single-Wall Nanotubes

A. V. Bazhenov, T. N. Fursova, I. O. Bashkin, V. E. Antonov,  
and I. V. Kondrat'eva

Institute of Solid State Physics, Chernogolovka,  
Moscow, Russia

A. V. Krestinin and Yu. M. Shul'ga

Institute of Problems of Chemical Physics, Chernogolovka,  
Moscow, Russia

**Abstract:** Carbon single-wall nanotubes (SWNTs) were loaded with 5.4 wt.% H by exposing to a hydrogen pressure of 50 kbar at 500°C. Investigation of the optical transmission spectra showed that the hydrogenation significantly suppressed the high-frequency conductivity  $\sigma$  of free carries in the SWNTs and also eliminated the band-to-band electronic transitions. Instead, a narrow line of the C-H stretching vibrational mode appeared at 2845 cm<sup>-1</sup>. A gradual removal of hydrogen from the hydrogenated SWNTs by vacuum annealing at  $T \geq 500^\circ\text{C}$  resulted in an approximately linear decrease in the intensity of this line with decreasing hydrogen content. This evidenced that most H atoms in the hydrogenated SWNTs were covalently bonded to the carbon atoms. The complete removal of hydrogen by vacuum annealing at 700°C partly restored  $\sigma$  and the intensity of the electronic transitions characteristic of the initial SWNTs.

**Keywords:** Carbon nanotubes, hydrogen, optical transmission spectra, diffuse reflection

SWNTs are known reversibly to absorb considerable amounts of hydrogen at moderate hydrogen pressures  $P$  and room or lower temperatures  $T$  that makes

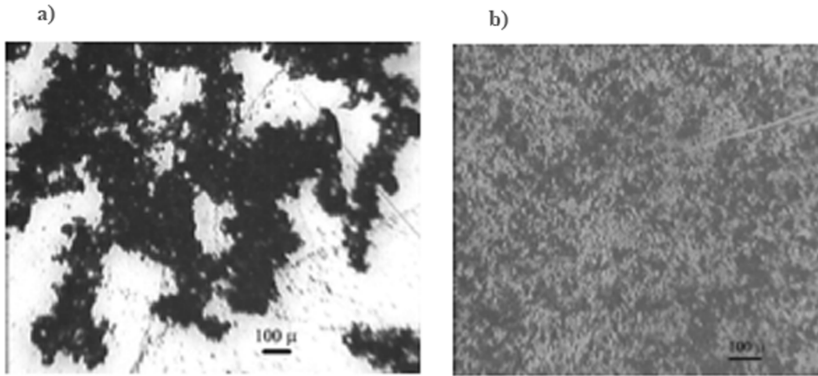
Address correspondence to T. N. Fursova, ISSP RAN, Chernogolovka, Moscow distr., 142432, Russia. E-mail: fursova@issp.ac.ru

these nanotubes a promising material for hydrogen storage (1). The dominating mechanism of hydrogen sorption at these  $P$ - $T$  conditions is physisorption of  $H_2$  molecules on the graphene layers of SWNTs (2). On the other hand, hydrogenation of SWNTs at a  $P = 90$  kbar and a  $T = 450^\circ\text{C}$  produced a new C-H compound containing 6.8 % H and thermally stable in vacuum at temperatures up to  $500^\circ\text{C}$  (3). To analyse the character of hydrogen bonding in this high-pressure compound, the IR diffuse reflection spectra were measured for the SWNTs in the initial state, after the hydrogenation and after a partial outgassing annealing in vacuum (3). The spectrum of the hydrogenated SWNTs showed a line at around  $2860\text{ cm}^{-1}$  typical of stretching vibrations of the C-H covalent bond. Surprisingly, this line vanished after the removal of less than a half of the hydrogen by vacuum annealing. This might indicate that the remaining half of the hydrogen atoms were in an unusual state silent in the IR spectra. However, the large absorption in SWNTs made a quantitative comparison of the line intensities difficult and therefore other techniques should have been applied to prove or disprove the effect.

In the present work, IR transmission spectra of the SWNT thin films and the IR diffuse reflection spectra of the SWNT powders were measured at room temperature in the range  $400$  to  $9000\text{ cm}^{-1}$  using a Fourier spectrometer. An IR microscope located the measuring area on the film surface. Transmission spectra of the thin films were also measured in the spectral range  $4000$  to  $18000\text{ cm}^{-1}$  using a standard double-beam spectrometer.

The SWNTs used for the hydrogenation were synthesized by an electric arc method using a nickel–yttrium catalyst. The purified batch contained 80–85 wt.% SWNTs. The SWNTs were loaded with hydrogen by exposing to a  $H_2$  pressure of 50 kbar for 18 h at  $T = 350^\circ\text{C}$  and then for another 6 h at  $T = 500^\circ\text{C}$ . The hydrogenation technique is described in (4). The hydrogen content  $x = 5.4$  of the compound was determined by combustion in a flow of oxygen at  $1400^\circ\text{C}$  followed by weighting the resulting  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This hydrogen content corresponds to the chemical formula  $\text{CH}_{0.7}$  and is lower than  $x = 6.8$  of the compound  $\text{CH}_{0.88}$  produced in (3) at a pressure of 90 kbar. The hydrogen solubility in SWNTs therefore shows significant pressure dependence.

To produce thin films, powder of the initial or hydrogenated SWNTs was dispersed in acetone by a 10-minute ultrasonic treatment. The prepared suspension was then dropped on a  $\text{SiO}_2$  or KBr substrate and dried. If the substrate had room temperature, the resulting films were inhomogeneous because the SWNTs got significantly aggregated while drying (Figure 1a). The rate of aggregation increased by an order of magnitude for the hydrogenated SWNTs. To get homogeneous films, the suspension was pulverized on substrates previously heated to  $100^\circ\text{C}$ . The preheating efficiently suppressed aggregation of both initial (Figure 1b) and hydrogenated SWNTs. Films of the initial SWNTs thus prepared were free of acetone, whereas a considerable amount of this solvent (presumably, physisorbed) still remained in the films of hydrogenated SWNTs and its intense absorption lines were clearly seen in the



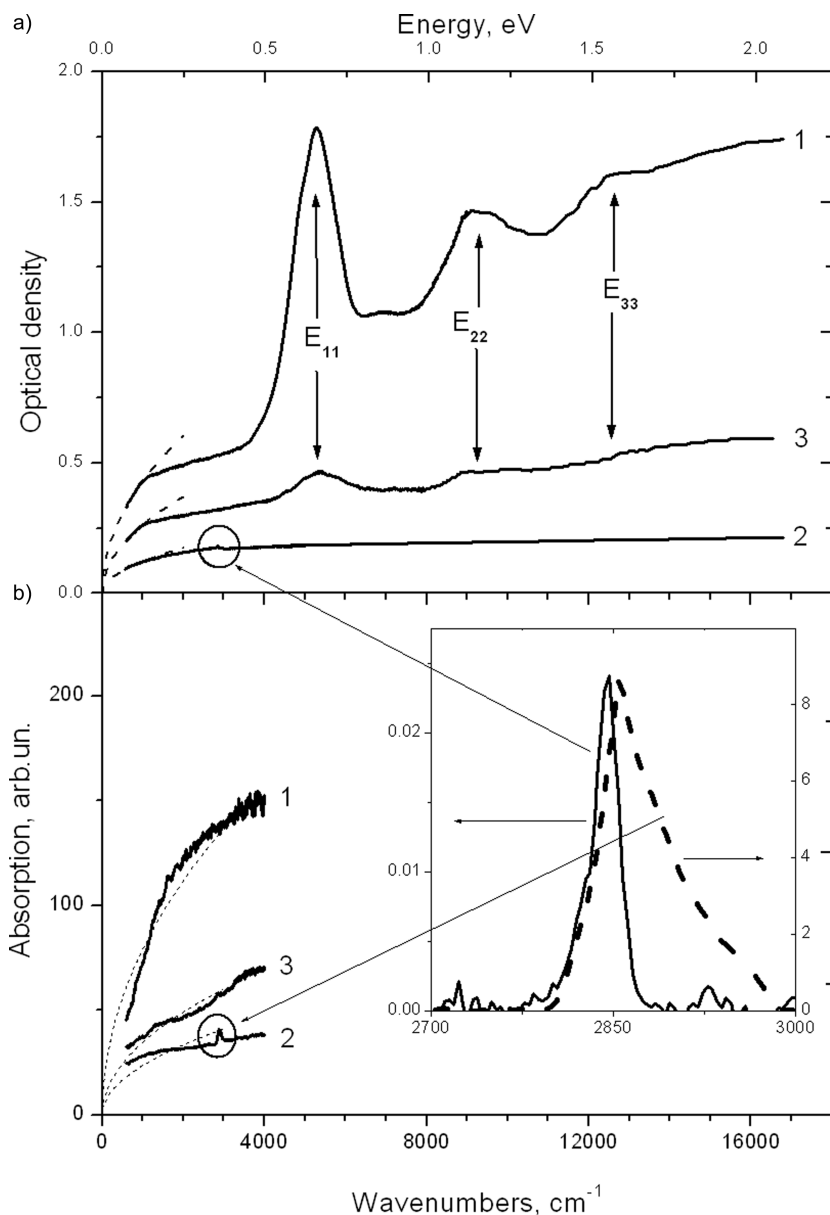
**Figure 1.** Optical microscope images of the thin films in the regime of the light transmission: a) solution of the SWNTs dispersed in acetone was dropped on the substrate and dried at room temperature; b) SWNTs dispersed in acetone were pulverized on the substrate heated to  $\approx 100^\circ\text{C}$ .

transmission spectra. To remove the acetone, films of the hydrogenated SWNTs were heated to  $150^\circ\text{C}$  in vacuum.

The optical density spectra of thin films (Figure 2a) and the absorption spectra of powders (Figure 2b) of the initial and hydrogenated SWNTs show a monotonic increase in the absorption with increasing photon energy in the spectral range  $400\text{--}4000\text{ cm}^{-1}$ . Taking into account that our samples should be a mixture of metallic and semiconducting SWNTs (5–7), this increase in the absorption is caused by high-frequency conductivity  $\sigma$  of free carriers. The Drude approximation of the low-energy part of the spectra gives  $\sigma = K^2c/(16\pi^2\nu)$  at wavenumbers  $\nu \ll \gamma$ , where  $\gamma$  is the scattering rate of free carriers and  $K$  is the absorption coefficient. Comparison of spectra 1 and 2 in both Figure 1a and Figure 1b shows that the hydrogenation decreases  $\sigma$  of the SWNTs by one order of magnitude.

The optical density spectra of thin films of the initial SWNTs also demonstrate distinct absorption peaks at 0.62, 1.13 and 1.65 eV (Figure 2a, spectrum 1). These transitions result from van Hove singularities in the density of electron states due to the one-dimensional nature of nanotubes (8). The first two lines are the transitions in the semiconducting SWNTs, the third line is the transition in the metallic SWNTs (9). The spectral position  $E_{11} = 0.62\text{ eV}$  of the first peak permits evaluating the average diameter  $d$  of the semiconducting SWNTs as  $d \approx 2a\delta/E_{11} \approx 1.2\text{ nm}$  in good agreement with the value 1.5 nm derived from the electron-microscopy data.

Peaks  $E_{11}$ ,  $E_{22}$  and  $E_{33}$  disappear after hydrogenation (Figure 2a, spectrum 2) and a new narrow line arises at  $2845\text{ cm}^{-1}$  (0.353 eV) as can be more clearly seen in the inset in Figure 2b. The new line indicates the formation of strong covalent C-H bonds in the samples. The absorption coefficient  $K$  of the SWNT powder can be calculated from the diffuse reflection  $R$

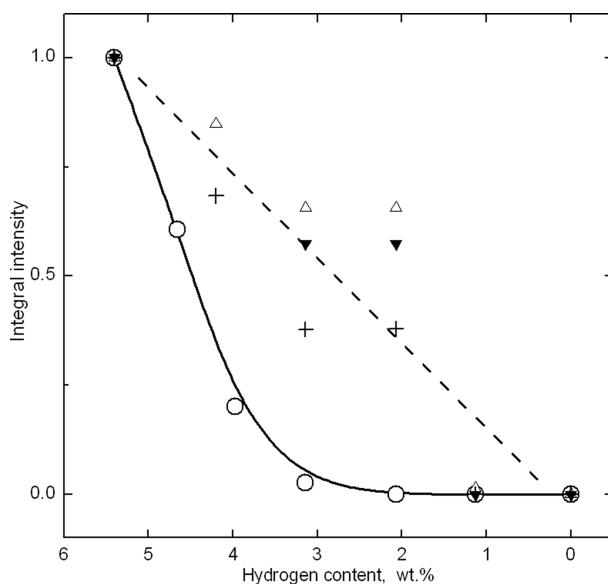


**Figure 2.** Optical density spectra of thin films (a) and absorption spectra restored from the diffuse reflection of powders (b) of the initial, hydrogenated and outgassed SWNTs (spectra 1, 2 and 3, respectively). The dashed curves in the low-energy part of the spectra represent the Drude approximation of the absorption spectra. The inset in Figure 2b shows the absorption lines of the C-H bonds in a thin film (solid curve) and powder (dashed curve) of the hydrogenated SWNTs.

using the Kubelka-Munk equation  $K = (1 - R)^2 s / (2R)$ , where  $s$  is the scattering coefficient. As seen from the inset in Figure 2b, the  $2845 \text{ cm}^{-1}$  peak in SWNT powder is significantly broadened.

Transfer of electrons from carbon to hydrogen may explain the observed decrease in the high-frequency conductivity and the disappearance of the electronic transitions in the spectra of hydrogenated SWNTs. This should lead to a decrease in the free carrier concentration and in filling of the highest occupied van Hove singularities. Is it possible? A significant reconstruction of the SWNT density of states due to the strongly bonded hydrogen cannot be excluded either. Besides, some defects appear in the structure of SWNTs and also decrease the light absorption. There are two reasons to think so. First, the complete removal of hydrogen by vacuum annealing at  $700^\circ\text{C}$  restores the high-frequency conductivity and absorption peaks only partly (compare curves 3 and 1 in Figure 2). Second, our control experiment showed that the electronic transitions vanish in the spectrum of SWNTs exposed to the same  $P$ - $T$  conditions without hydrogen. These defects may decrease mobility of free carriers (localization of free carriers?) and disturb one-dimensional structure of the electron states.

A few SWNTs samples with intermediate hydrogen contents were prepared by partial outgassing of the hydrogenated material in an evacuated volume at  $T \approx 500^\circ\text{C}$ . Figure 3 presents the integral intensities of the



**Figure 3.** Integral intensity of the  $2845 \text{ cm}^{-1}$  line in the IR absorption spectra of powder (open circles) and thin films (other symbols) of the hydrogenated and partly outgassed SWNTs as a function of their hydrogen content. The dashed line represents the linear fit to the data for thin films.

2845  $\text{cm}^{-1}$  line in the IR spectra of the partly outgassed samples as a function of the hydrogen content. Results for the thin films show a significant scatter but, if averaged, give a linear dependence (dashed line in Figure 3) that indicates proportionality of the peak intensity to the hydrogen content of the film. Such proportionality suggests that most H atoms in these films were covalently bonded to carbon atoms. The intensity of the 2845  $\text{cm}^{-1}$  line calculated from diffuse reflection steeply decreases on outgassing and significantly deviates from the linear dependence. This discrepancy can be explained assuming that powder particles in the partly outgassed SWNTs were inhomogeneous and their outer layers were depleted in hydrogen. In fact, diffuse reflection can only feel a very thin surface layer of the particles due to the large value of the absorption coefficient  $K \approx 10^4 \text{cm}^{-1}$  for SWNTs, while the measured intensity is related to the mean hydrogen content of the material.

## ACKNOWLEDGMENTS

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